Thin Solid Films 403–404 (2002) 320–324
www.elsevier.com/locate/tsf

The change of the electronic properties of CIGS devices induced by the 'damp heat' treatment

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Abstract

The changes of the electronic properties of the absorber layer in the ZnO/CdS/Cu(In,Ga)Se_2 photovoltaic devices induced by the 'damp heat' test have been investigated by use of junction capacitance techniques. Deep level transient spectroscopy and admittance spectroscopy have been employed for characterization of the bulk and interface levels in the absorber. Additional information on the transport mechanisms has been provided by the analysis of current–voltage characteristics. We conclude that the 'damp heat' treatment introduces deep electron traps, thus increasing the absorber compensation and decreasing V_{oc} of the devices. The same states facilitate transport of carriers by means of trap-assisted tunneling, causing a decrease of the fill factor. O_{Se} is a probable candidate for a defect introduced by the humidity test.

Keywords: Cu(In,Ga)Se_2; Damp heat; DLTS; Admittance spectroscopy; Trap levels

1. Introduction

Thin film solar cells based on Cu(In,Ga)Se_2 (CIGS) are on the threshold of commercialization for terrestrial use, therefore not only their conversion efficiency but also a long term stability under environmental conditions is an important issue. In recent years several tests on stability have been performed [1–3]. These investigations have shown that humidity-induced cell degradation is related to two factors: (1) changes induced in the front contact and window area; and (2) changes of the electronic properties of the absorber layer. Both lead to a decrease of the fill factor (FF) and V_{OC}, having almost no impact on I_{SC}.

ZnO/CdS/Cu(In,Ga)Se_2 unprotected cells have been subjected to a standard 'damp heat' (DH) test and investigated by Wennerberg et al. [2] with a special emphasis put on the first of the above-mentioned issues. An increase of the ZnO sheet resistance and a degradation of the grid have been observed. However, these factors could not explain all of the observed V_{oc} and FF loss. In the present work a complementary investigation of the same samples is presented, but this time it is focused on the change of the electronic properties of the absorber caused by the DH treatment. DLTS and admittance spectroscopy have been used with the aim to probe the changes of the interface and bulk defect spectra of these devices induced by the exposure to humidity at elevated temperature. The influence of white light soaking on the DH devices have also been investigated.

2. Experimental details

The samples under investigation are ZnO/CdS/Cu(In,Ga)Se_2 structures with a coevaporated absorber and a CBD-deposited CdS buffer. The details of the solar cells preparation, their photovoltaic parameters and testing procedure are given in Wennerberg et al. [2]. The data presented here have been obtained for cells subjected to 1000 h of 'damp heat' (85% relative humidity at 85°C) and for untreated devices, indicated as 'baseline' in the text. As found in Wennerberg et al. [2], the efficiency of the cells, initially equal to 14%,

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0040-6090/02/$ - see front matter
PII: S0040-6090(01)01510-3

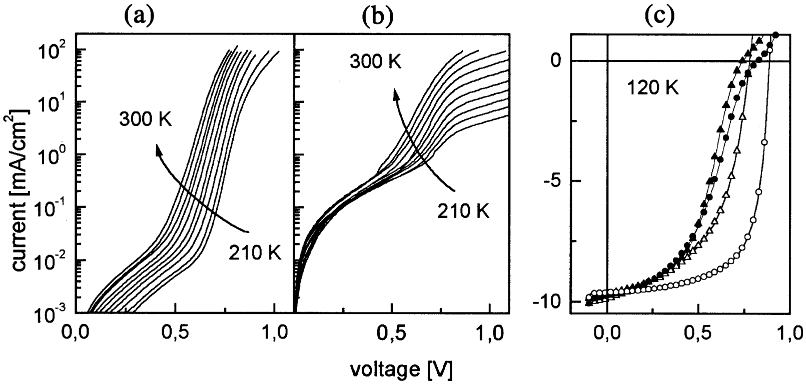

Fig. 1. Current–voltage characteristics: (a) in the dark for the baseline cell in the temperature range 210–300 K; (b) the same for the DH cell; (c) *I–V* characteristics under red illumination at 120 K for the baseline (circles) and DH device (squares). Full symbols correspond to the results in a relaxed state and open symbols — after white light soaking.

dropped to approximately 9% after DH treatment (V_{OC} decreased approx. 20% and FF almost 15%).

DLTS has been performed by use of a DLS-82E capacitance bridge. We have employed two modes of operation for DLTS spectra acquisition: a temperature scan at a fixed emission rate window and a frequency scan at a constant temperature with the emission rate window changing continuously from 1 to 2000 Hz. In the DLTS measurements we have routinely used 0.5 V pulses in the forward direction applied to zero-biased devices. In a variation of standard DLTS — reverse-bias DLTS (RDLTS) the same pulse height in the reverse direction on zero-biased device has been used. The latter method is known to provide information on the trap states located in the interface region of the structure [4].

A Hewlett Packard HP4284A admittance meter has been employed for measurements of the admittance spectra in the frequency range 100 Hz–1 MHz.

White light soaking has been performed by illumination with a halogen lamp at room temperature for 1 h. Measurements under red (absorbed only in CIGS) illumination have been made by use of the light filtered through a 0.4-mm CdS platelet.

3. Results

3.1. Current–voltage characteristics

An analysis of the dark current–voltage characteristics (Fig. 1a,b) reveals a change in the transport mechanism arising after the DH treatment. The diode ideality factor increases substantially after DH and shows strong dependence on the temperature indicating that trap-assisted tunneling replaced thermally activated emission characteristic for the untreated high efficiency device. The increase of the series resistance and shunting current might be explained to some extent by the contact degradation and humidity-induced leakage due to grain boundaries but also might be a feature related to the changes of the absorber electronic properties.

In Fig. 1c the *I–V* curves under red illumination and at low temperature are shown. According to Zabierowski and co-workers [5,6] this type of measurement reveals an influence of the p^+ layer close to the heterointerface. The curves for both devices in the relaxed state are quite similar. However, after white light soaking the improvement of the photovoltaic parameters V_{oc} and FF is much more prominent for the baseline than DH device.

3.2. Junction capacitance spectroscopy

The admittance spectra for the DH and baseline devices are shown in Fig. 2. For the sake of clarity they have been recalculated to the dependence of the space charge width W on frequency. High frequency depletion layer width increased after DH from approximately 0.6 μm in baseline devices to a value exceeding the width of the absorber layer. Thus the net shallow acceptor concentration has been reduced by the treatment by approximately an order of magnitude.

The step in the admittance spectra observed between 100 and 240 K in the baseline device (see Fig. 2a) corresponds to the emission from electron traps situated at or close to the interface (N1) [7]. This process is also observed in the DH sample over a similar temperature range. In the differentiated spectrum (Fig. 2c) the N1 trap is revealed as a series of small peaks in the upper (low temperature) part of the spectrum. Apart from N1, in the DH device a second step at higher temperatures (N2), not detected in the untreated device, has been observed.

N1 and N2 levels are also present in the RDLTS and DLTS spectra, as shown in Fig. 3a: a minority carrier signal for the interface peak in both samples and a majority signal for N2 occurring only in the DH device.

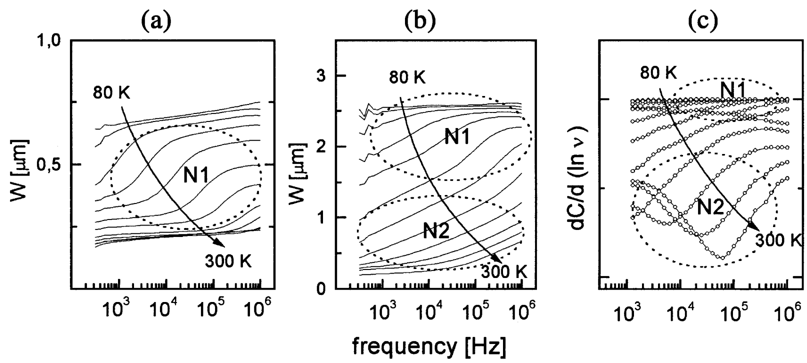

Fig. 2. Admittance spectra in the temperature range 80–300 K: (a) baseline device, (b) DH device. (c) Differentiated spectra for the DH device.

An additional feature in the DH cell is also a large peak above 300 K (N3), corresponding to an electron trap too deep to be detected by admittance spectroscopy.

The DLTS results obtained by both frequency and temperature scans provide similar results for the N3 peak (see Arrhenius plots in Fig. 4b), but significant differences have been observed for the N2 level. This is illustrated in Fig. 3b,c, where the sets of frequency and temperature scans for the N2 process are shown. While the frequency scans give very broad spectra with barely discernible minima hardly shifting with temperature, temperature scans feature much better resolved peaks. The frequency scan is in principle a more straightforward method of determining the emission rates from trap levels at a given temperature, so this observation brings in to question a simple interpretation of the N2 peak as related to the thermal emission of holes from a bulk hole trap.

4. Discussion

4.1. Interface states

The activation energy related to the N1 peak corresponds to the energetical distance of the Fermi level from the conduction band at the interface with some contribution from bulk donors modified by a strong electric field [7–9]. In Fig. 4a the Arrhenius plots of emission rates from the interface traps determined by admittance and RDLTS for the baseline and the DH device in the relaxed and light-soaked state are shown. We find that in the relaxed state the results are very similar for both devices featuring the activation energy at high temperatures, approaching approximately 0.2 eV. At lower temperatures the curves reveal increasing influence of the electric field enhanced emission [8,9]. The difference arises in the white light-soaked state: for the baseline cell high-temperature activation energy

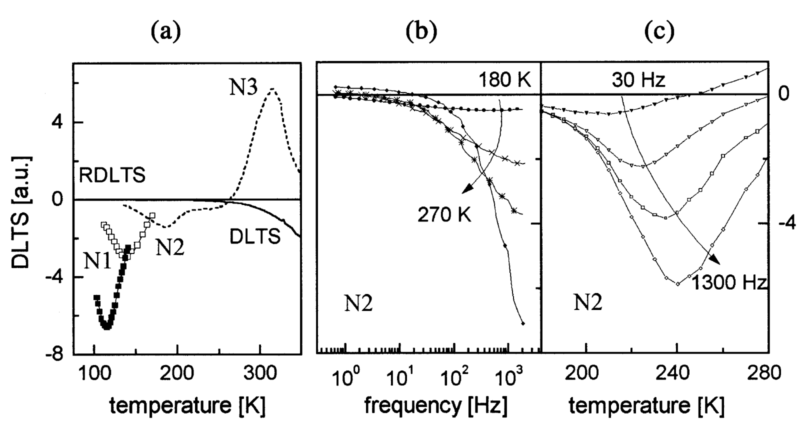

Fig. 3. (a) DLTS spectra for a baseline (continuous line) and a DH (dotted line) device obtained at the emission rate window of 25 Hz, shown together with the RDLTS spectra (emission rate window 1000 Hz; full symbols, baseline cell; open symbols, DH cell). (b) DLTS frequency scans for the N2 level in the temperature range 180–270 K. (c) DLTS temperature scans for the N2 level obtained at emission rate windows between 30 and 1300 Hz.

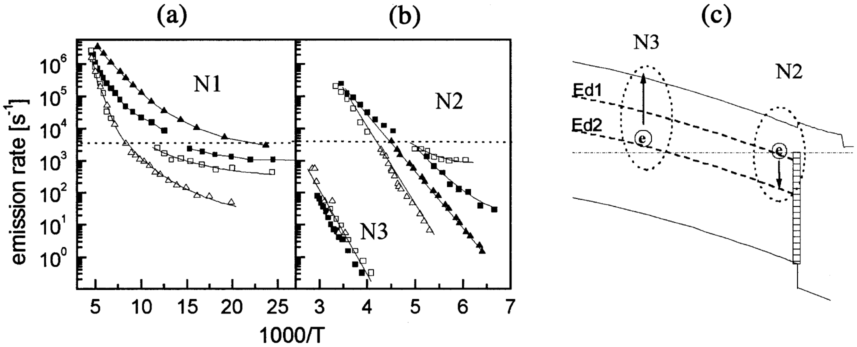

Fig. 4. (a) Arrhenius plots of emission rates for the N1 peak: baseline device-triangles, DH device, squares. (b) Arrhenius plots of emission rates for the peaks N2 and N3: frequency scans, squares; temperature scans, triangles. Open symbols correspond to the data obtained in the relaxed state of the devices, full symbols to the data in the light-soaked state. Results obtained from admittance measurements are shown above the broken line. (c) A diagram showing the electron emission corresponding to N3 level and electron capture revealed as the N2 level.

approaches 60 mV, while in the DH sample we observe increased distortion by the electric field rather than a decrease of the activation energy. This means that the beneficial effect of the white light interpreted in Igalson et al. [6] as resulting from a reduction of the p+ layer close to the interface, is not as pronounced here as in the efficient cells. This agrees with the behavior of the illuminated *I–V* curves, which also show that DH samples are less sensitive to light soaking.

4.2. Bulk states

A new feature in the DLTS spectrum of the DH devices is a large positive peak at temperatures above 300 K (N3). The emission rates for that peak do not depend meaningfully on the method used (temperature or frequency scan) or state of the sample (relaxed or light soaked) (Fig. 4b). Thus we interpret N3 as a bulk electron trap, which has been introduced by the DH treatment. The trap depth estimated from the Arrhenius plot is 0.55 ± 0.05 eV. In our opinion this is a defect responsible for the increase of the compensation degree observed in DH devices.

The hole trap N2 is a well-known property observed often in the admittance and DLTS spectra of less efficient devices. It features activation energy in the range of 0.25–0.4 eV and a broad distribution of emission rates, which have been explained by the energetical distribution of levels centered at energy of approximately 0.3 eV [10]. It has been shown that electron irradiation increases N2 signal intensity [11]. Also, the study of humidity-tested cells prepared at IPE, Stuttgart, revealed an increase of this signal [3]. Since the apparent concentration of the N2 trap correlates well with the efficiency of the CIGS devices, it has been suggested that this is a major recombination center in these cells [12].

Here we propose a different explanation of the N2 process. First, we note that the inconsistency between the results of temperature and frequency scans might be expected if a *capture* and not *emission* process is being measured. Capture features broad distribution of the time constants, but DLTS processing during temperature scan selects only those, which occur at the Fermi-level position. Therefore from the temperature scan a well-defined activation energy is also obtained for the capture process [13]. Evidently, this sort of behavior has been observed in DLTS for the N2 peak (Fig. 4b). We conclude that the N2 feature is due to the *capture of electrons* by deep traps (N3), which have been emptied by the forward pulse and not by the *emission of holes*. This would be possible if some shallower defects participate in the electron transfer from the interface to deeper states. The proposed process of the electron capture resulting in the N2 signal is illustrated in Fig. 4c. Then the activation energy for the N2 peak would correspond roughly to that of shallower donors, provided the trap-to-trap electron transfer is weakly temperature-dependent. If we have in mind, that In_{Cu} compensating donors are in abundance in the CIGS layer, the electron transfer between In_{Cu} and N3 seems to be quite probable. We notice that the activation energy for the N2 peak agrees very well with the theoretical predictions for the In_{Cu} defects [14].

5. Conclusions

The main effect of the DH treatment on the absorber layer is a creation of midgap donor-type defects. This causes an increase of the compensation level and seems to be responsible for both V_{oc} and FF loss. Open circuit voltage decreases because of a decrease of the electric field in the junction and an increase of the total concentration of the recombination centers. Furthermore, N3 states together with other compensating donors In_{Cu}, facilitate the transport via trap-assisted tunneling. That leads to the increase of diode ideality factors causing a decrease of both FF and V_{oc}.

A large N2 signal detected in DH, as well as in other less efficient devices indicates in our opinion, that a large concentration of deep traps is present in the absorber. They are able to capture electrons via In_{Cu} antisites producing a signal featuring the DLTS sign as for the emission of holes. This approach explains a puzzling experimental observation that the same level — the N2 hole trap — seems to be introduced by very different treatments as an electron irradiation and humidity test. From the point of view of our model different deep centers might be responsible for the N2 signal observed in humidity-tested and irradiated devices.

The origin of the N3 level introduced by the 'damp heat' treatment may only be a subject of speculation at present. The O_{Se} defect is a plausible candidate, since according to a theoretical prediction it is a deep donor [15].

Acknowledgements

This work was supported by the Dean of the Faculty of Physics of Warsaw, University of Technology. The authors are grateful to Mr Lukasz Posepny for carrying out the admittance measurements.

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